Summary

Optically active Betti base [1-(α-amino benzyl)–2–naphthol] also known as 1,3–amino naphthols (Fig. 1) and its derivatives have been used in various organic transformations viz. catalytic asymmetric alkylation, alkenylations, Michael additions, Aldol reactions and cyclopropanations.

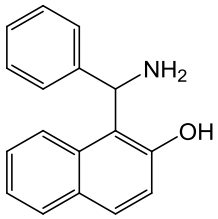

Figure 1 Betti base

Amino phenols with similar structural entity as that of Betti base are involved in various natural processes. Most of the natural processes are redox in nature in which electron & proton transfer takes place simultaneously (proton coupled electron transfer, PCET). Hence the electrochemical properties of amino phenols have been expensively studied. The electrochemical properties of Betti base have yet been described in the literature.

Betti base with sp^3 hybridized carbon attached to phenyl ring, amine and naphthol, is expected to exhibit interesting redox properties. Hence in the **Chapter 2**, synthesis, characterization and electrochemical properties of Betti base is reported. The voltammetric results are further analyzed with elimination methods. The combination of CV and elimination voltammetry has emerged as an amazing tool to identify the redox processes of electroactive compounds. It can be concluded from the CV and EVLS data that the Betti base and its derivatives are electroactive and undergo irreversible redox process.

It is evident that, to understand the role of Betti base in ligand accelerated reactions in presence of metal salt, isolation and characterization of the metal complex is essential. Betti bases with better ligating groups are expected to act as an excellent ligand for coordination with transition metal ions. Copper(II) complexes with redox active amino phenols have been widely studied as a model for galactose oxidase (GAO). The redox and catalytic properties of Cu(II) complexes with various amino

phenols have been exhaustively studied. So in the **Chapter 3** the synthesis, characterization and electrochemical properties of Cu(II) complexes with Betti base and its derivatives are reported. Betti base and its derivatives coordinate to Cu(II) ion with 1:2 stoichiometry, the complexes with racemic ligand were found to be achiral while the complexes with optically active ligands resulted in formation of enantiomers with more distortion in the geometry as confirmed by EPR analysis. The single crystal structure of Cu(II) complex with $\mathbf{L_1}$ is shown in Fig 2a. The proposed structure of Cu(II) complex with $\mathbf{L_2}$ is shown in Figure 2b.

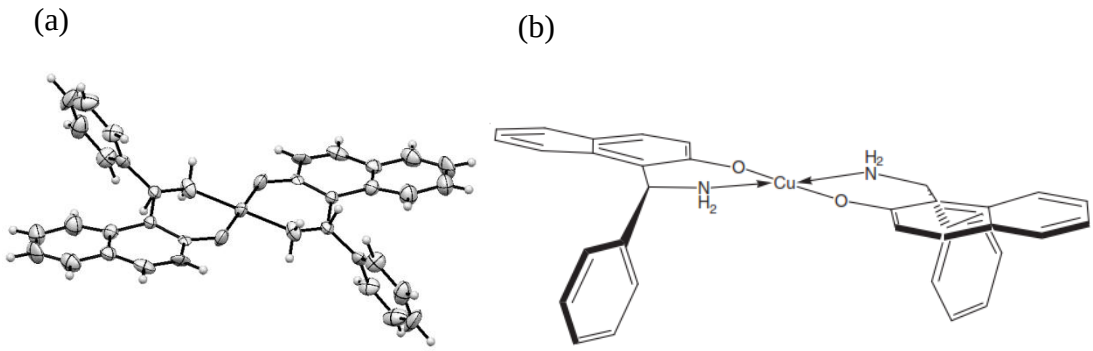

Figure 2 (a) single crystal X-ray analysis of **Cu1 (b)** proposed structure of **Cu2**

The cyclic voltammetric analysis revealed that the synthesized complexes undergo quasireversible redox process. Due to redox active nature of the Betti base the electrochemical oxidation of metal center Cu(I)→Cu(II) is not observed (Fig. 3) presumably due to intramolecular electron transfer process between metal to ligand to form more stable Cu(II) species. The CV results are further analyzed by elimination voltammetry.

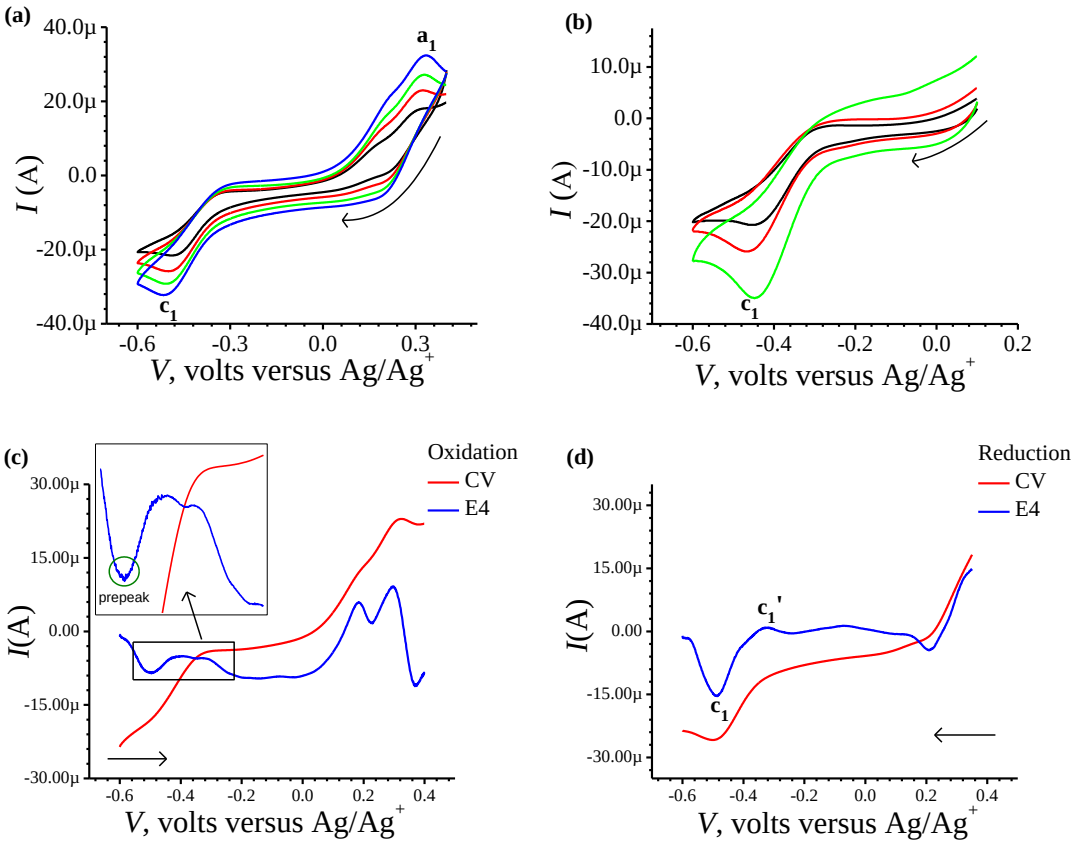

Figure 3 (a),(b) CV of Cu2 (c) E4 curve for oxidation of **Cu2** (d) E4 curve for reduction of **Cu2**

The analysis of electrochemical data indicates ligand centered oxidation and metal centered irreversible reduction suggesting noninnocent behavior of the ligand.

Chapter 4 deals with the application of Cu(II) Betti base complexes as a catalyst for the asymmetric epoxidation of styrene. The Cu(II) complexes are known for single electron transfer organic processes. However the redox active Betti base after being coordinated with Cu(II) ion should behave noninnocently. To check the noninnocent behavior of coordinated Betti base, a two electron transfer reaction namely epoxidation of styrene was studied with Cu(II) complex with Betti base as catalyst.

The catalysed reactions yield high conversion in polar aprotic solvents i.e. ACN and DMSO. The reaction in DCM yield low oxidized product of styrene. The study of isolated catalyst after reaction indicated distorted geometry with activation of –C–H bond α to nitrogen.

The –C–H bond activation of the catalyst during catalysis process makes the catalyst optically inactive which ultimately failed to induce asymmetry.

The role of DMSO is found to be very crucial in enantioselective catalytic process. The formation of 2-oxo-2-phenyl acetaldehyde by oxidation of styrene epoxide was confirmed by chiral GC-MS analysis of the reaction mass. The enhanced enantioselectivity in DMSO is attributed to catalyzed asymmetric epoxide ring opening. The redox property of **Cu1** complex in DMSO is different than that in ACN. (Fig. 4)

The current for the reduction and oxidation process in DMSO increased drastically in second cycle of the CV. The increase in current in second CV cycle for the redox process of **Cu1** in DMSO presumably due to synergistic interaction of coordinated ligand with metal center, such behavior of the ligand was not observed when the CV was recorded in the ACN. [Fig. 4(b)]

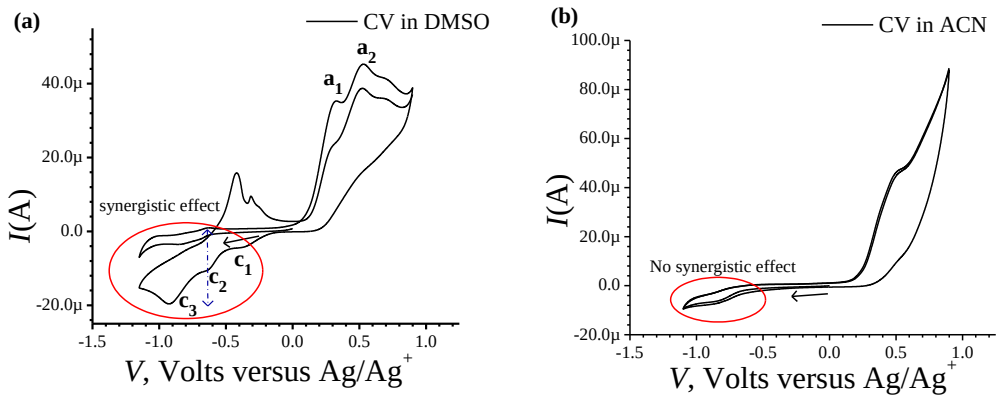

Figure 4 (a) CV of **Cu1** in DMSO (5 mmol) (b) CV of **Cu1** in ACN (5 mmol)

The role of solvent particularly DMSO is found to be very crucial in enantioselective catalytic process. DMSO tunes the electronic environment around metal ion which would be responsible for both C-H and N-H bond activation in presence of TBHP which resulted in moderate to high conversion of styrene (up to 80 %) with high enantioselectivity (up to 80%) towards *R*- Styrene epoxide through selective ring opening of *S*-styrene epoxide.

The enhanced catalytic activity under mild conditions presumably due to the noninnocent behavior of the Betti base acting as <u>spectator</u> ligand.

Chapter 5 deals with the stereoselective cyclopropanation of styrene. The Cu(II) complexes with racemic mixture of ligands are found to be more efficient.

In cyclopropanation reaction Cu(II) Betti base complexes with square planar geometry are stereoselective towards cis product while the complexes with distorted geometry selectively produce trans product.

The square planar geometry along with steric hindrance of the coordinated ligand of the complexes **Cu1** and **Cu8** facilitated styrene to approach parallel to the metal carbene adduct, giving 40% cis product through cyclic mechanism. On the other hand complexes with distorted geometry forced styrene to take parallel approach resulting in formation of trans product through asynchronous open mechanism. On the basis of the catalytic results, the probable pathway for the formation of metal-carbene adduct has been proposed as in Figure 5.

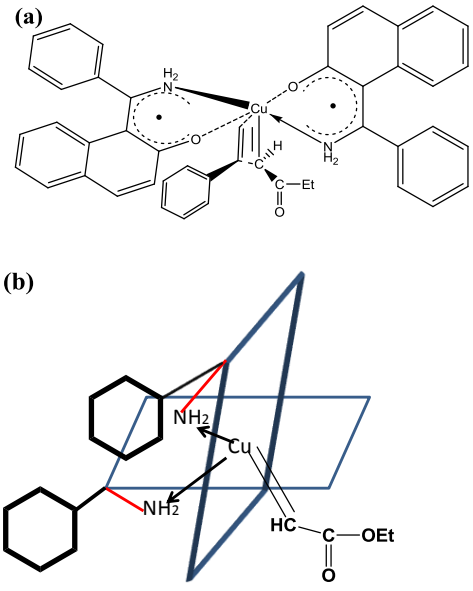

Figure 5 Probable pathway for the formation of metal-carbene adduct